103. *The Sensitisation of the Hydrogen–Oxygen Reaction by Nitrous Oxide.*

By C. J. DANBY and C. N. HINSHELWOOD.

If nitrous oxide is added last to hydrogen–oxygen mixtures at 550°, it behaves as an inert gas, but if oxygen is added last to a mixture of nitrous oxide and hydrogen, immediate ignition occurs. The cause of this phenomenon is traced to the production from nitrous oxide and hydrogen of nitric oxide in amount below that detectable by ordinary analytical methods. A mechanism for its formation is discussed.

If nitrous oxide is added to a mixture of hydrogen and oxygen at 550° it behaves essentially as an inert gas. (The detailed evidence for this statement is given in Section 1 of the experimental results below.) If, however, nitrous oxide and hydrogen are mixed, and oxygen is added subsequently, there is either an immediate ignition or an autocatalytic reaction which eventually passes into an explosion. This remarkable influence of the order of addition seemed worthy of investigation.

Some sensitiser for the hydrogen–oxygen reaction must be formed from nitrous oxide and hydrogen; and its formation must be inhibited or retarded by the presence of oxygen. This is clearly shown by the results given in Section 2 : explosion occurs the more readily (*a*) the longer the nitrous oxide and hydrogen have been alone together, and (*b*) the smaller the pressure of the oxygen finally added.

The sensitiser proves to be nitric oxide, present in amount below that detectable by the sensitive diphenylamine test, but demonstrable by a special method described in Section 3.

The factors determining the explosion lead to a hypothesis about the mechanism of the nitric oxide formation; they can also be brought into relation with the sensitisation by ammonia of the hydrogen–oxygen reaction. Throughout the experimental study of this problem certain surface effects appear; these have had to be studied and, in the process, fresh information about the surface effects in the unsensitised reaction has been obtained (Sections 4 and 7).

For brevity it is assumed that necessary reference will be made to previous papers on the hydrogen–oxygen reaction (Hinshelwood and Williamson, " The Reaction between Hydrogen and Oxygen," Oxford Univ. Press, 1934) : but the following essential facts may be repeated : (*a*) at 550° hydrogen and oxygen give a slow reaction when the pressure is above the " upper limit " of an explosion area, (*b*) if the pressure is reduced, explosion occurs sharply at a given pressure, (*c*) minute amounts of nitric oxide may cause immediate ignition.

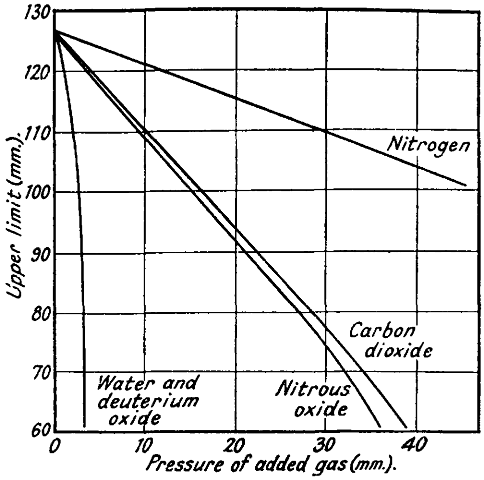
EXPERIMENTAL.

The apparatus consisted essentially of a silica reaction bulb heated in a horizontal electric furnace provided with a window for observing any explosion or ignition. The temperature was accurately maintained at 550° by means of a thermoregulator. The reaction bulb was connected to a mercury manometer, to reservoirs containing the various reagents stored over mercury, and to the usual system of pumps.

Hydrogen and oxygen were obtained from cylinders and were dried by phosphoric oxide. Nitrous oxide from a cylinder was condensed in a trap cooled in liquid air, and was then fractionated into an evacuated storage vessel. Provision was made for the withdrawal of samples of reactant gas from the bulb for analysis.

Upper explosion limits were determined by the " withdrawal " method of Thompson and Hinshelwood (*Proc. Roy. Soc.*, 1929, *A*, **122**, 610). The slow reaction at higher pressures was followed manometrically.

FIG. 1.



Influence of nitrous oxide on the upper limit at 550° *compared with that of other gases.*

1. *Evidence that Nitrous Oxide, when added last, behaves as an Inert Gas.*—Nitrous oxide can be added in any proportion to hydrogen–oxygen mixtures at 550° without apparent reaction, and determinations of the position of the upper limit can be made by the " withdrawal " method. Fig. 1 shows that the depression of the limit by nitrous oxide is almost exactly the same as that caused by carbon dioxide. Under these conditions, therefore, nitrous oxide behaves as an inert gas.

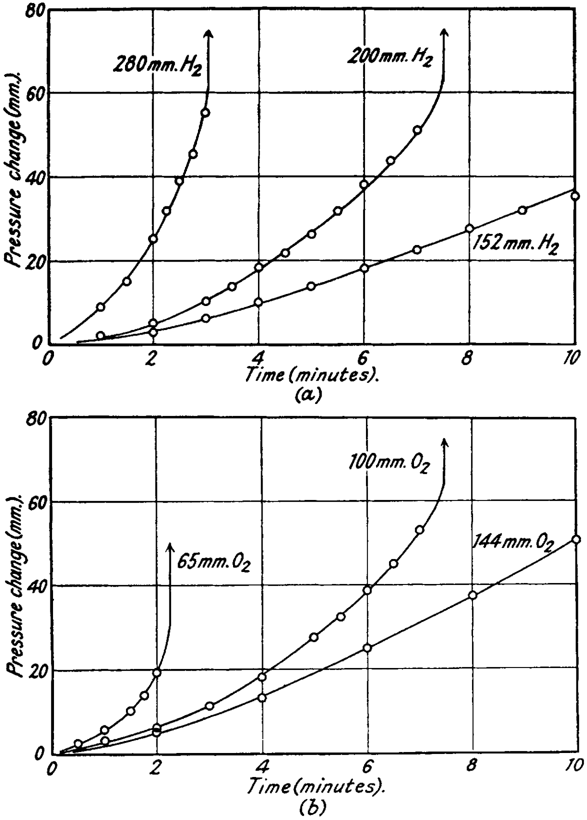
In a similar way small amounts of nitrous oxide added last to hydrogen–oxygen mixtures have practically no effect on the course of the slow reaction at higher pressures.

2. *Experiments on the Addition of Oxygen to Mixtures of Nitrous Oxide and Hydrogen.*—Slow

addition results in immediate ignition. If the nitrous oxide and hydrogen have not stood long and the oxygen is added rapidly, there is no explosion at first. Instead, however, of the normal slow reaction, there is an autocatalytic reaction which builds up to explosion in the manner shown in Fig. 2. This explosion occurs the sooner (*a*) the greater the concentration of nitrous oxide or of hydrogen, (*b*) the smaller the concentration of oxygen, and (*c*) the longer the nitrous oxide and hydrogen have been in contact. These facts are shown by the curves in Figs. 2 and 3.

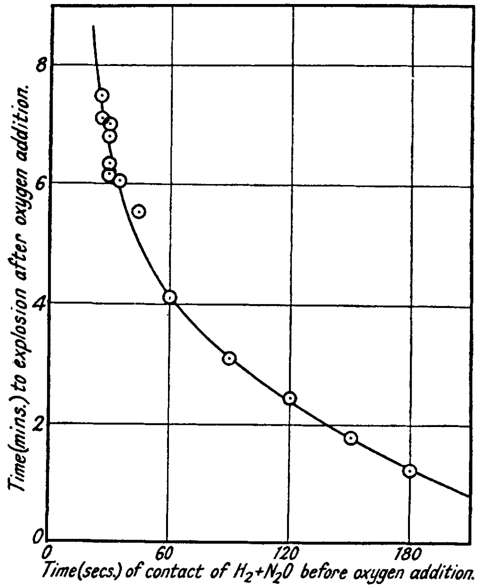
In a mixture to which oxygen had been added last, the upper limit is displaced to higher pressures, *i.e.*, the mixture is more explosive and the nitrous oxide is no longer behaving as an inert gas (contrast Section 1).

FIG. 2.



Influence of concentrations on the sensitised reaction. Upper graph : $N_2O = 45$ *mm.,* $O_2 = 100$ *mm., variable* H_2. *Lower graph :* $H_2 = 200$ *mm.,* $N_2O = 45$ *mm., variable* O_2. *Explosion occurs at points marked by arrows. The graph for variable* N_2O *resembles that for variable* H_2.

FIG. 3.



3. *Identification of the Sensitiser formed from the Nitrous Oxide and Hydrogen.*—Tests with reagents for nitric oxide, ammonia, hydrogen peroxide, and hydroxylamine all gave negative results. Either, then, the sensitisation is due to a substance present in too small amount to be detected, or it is due to something adsorbed on the walls and not removed when samples are taken for test. That it is in fact due to a stable substance present in the gas phase was proved by withdrawing a mixture of nitrous oxide and hydrogen which had reacted long enough to give the sensitiser, and storing it in a gas reservoir. The walls of the reaction vessel were in the meantime shown to be free from special activity. The sample was then returned to the reaction vessel and oxygen rapidly added. The immediate ignition produced showed that the sensitiser had been withdrawn with the gas, and had survived storage. Similar samples were then treated with various reagents. The only one which was found to remove the activity was

ferrous sulphate solution, whence it is concluded that the sensitiser is nitric oxide. The mechanism of its formation is discussed in Section 5.

4. *Surface Effects.*—The reaction of hydrogen and oxygen at higher pressures is a chain reaction occurring in the gas phase : the chains, however, end, and probably start, on the vessel wall. The rate of reaction both of the unsensitised and of the sensitised reaction depends very much on the state of the vessel wall, and in a way which is similar enough for the two reactions to show that important stages must be common to both.

In each, starting with a well evacuated vessel, the rate increases in successive experiments in a way that suggests that an adsorbed water film is being gradually built up on the silica surface, and that when this film is present chains start more easily or are broken less easily.

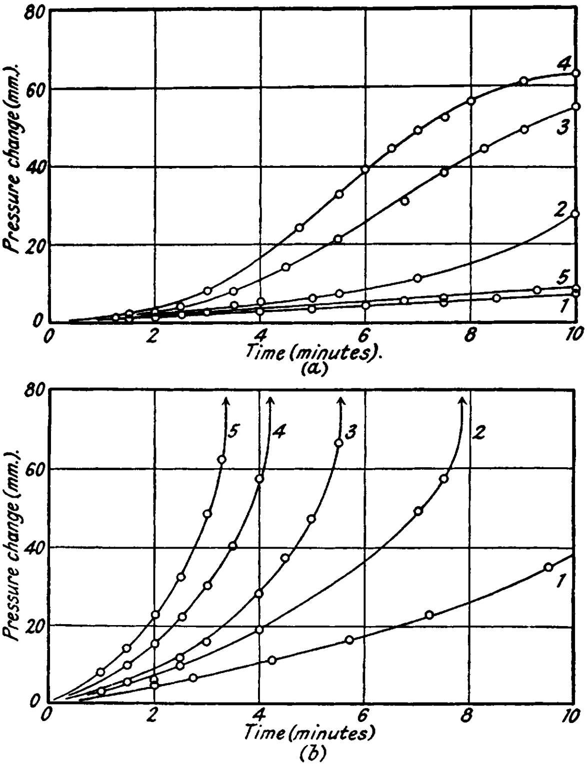


FIG. 4.

Variation in reaction rate in successive experiments due to surface effects. (a) *Unsensitised reaction* (H_2 = 200 *mm.*, O_2 = 100 *mm.* ; *temp.* 550°). (b) *Reaction sensitised by* N_2O (H_2 = 200 *mm.*, O_2 = 100 *mm.*, N_2O = 45 *mm.* ; *temp.* 550°). *The numbers indicate the order in which experiments were made. In* (a) *before* 5 *the vessel was evacuated at* 900° *to restore its original state.*

Some results are shown in Fig. 4. For the experiments described in Section 2, a standardised technique ensured reproducible conditions.

5. *Discussion of the Nitric Oxide Formation.*—Nitrous oxide yields the sensitiser, nitric oxide, presumably by interaction with some chain carrier of the nitrous oxide–hydrogen reaction. According to Melville (*Proc. Roy. Soc.*, **1933**, *A*, **142**, 524), the latter takes place as follows :

$$\begin{array}{llll} N_2O & = N_2 + O & \qquad H + N_2O & = N_2 + OH \\ O + H_2 & = OH + H & \qquad OH + H_2 & = H_2O + H \end{array}$$

The radicals which are possibly responsible for the formation of nitric oxide are O, OH, and H. Increase in the oxygen concentration in a system containing hydrogen will increase the concentration of OH and O by favouring the normal hydrogen–oxygen chain. But the formation of nitric oxide is inhibited by oxygen : whence it seems that only the hydrogen atom can be responsible, and we have to assume a mechanism starting with the process $N_2O + H =$

NO + NH. This process must be a slow one, the formation of the sensitiser being in fact gradual.

In the absence of oxygen we have :

(1) $N_2O + H_2 = N_2 + OH + H$ (Rate F_1)
(2) $H + N_2O = N_2 + OH$ (Constant k_2)
(3) $OH + H_2 = H_2O + H$ (,, k_3)
(4) $N_2O + H = NO + NH$ (slow) (,, k_4)

When oxygen is present in the system it competes with the nitrous oxide for reaction with hydrogen atoms. The most probable scheme being taken for the hydrogen–oxygen reaction, the following steps must then also be taken into consideration :

(5) $H + O_2 + M = HO_2 + M$ (Constant k_5)
(6) $HO_2 + H_2 = H_2O + OH$ (,, k_6)
(7) $HO_2 \longrightarrow$ destroyed at wall (,, k_7)

These equations lead to the expression

$$\frac{d\,[NO]}{dt} = \frac{F_1 k_4\,[N_2O]}{k_5[O_2][M]\left\{1 - \dfrac{k_6[H_2]}{k_6[H_2] + k_7}\right\}}$$

This equation predicts that in the presence of oxygen the rate of formation of nitric oxide will be increased by raising the nitrous oxide concentration, and reduced by raising the oxygen concentration. The greater the hydrogen concentration becomes, the more nearly the term $k_6\,[H_2]/(k_6[H_2] + k_7)$ approaches unity, hence the more nearly the denominator approaches zero. Increase in the hydrogen concentration will therefore raise the rate of formation of nitric oxide. These conclusions are in agreement with the experimental observations.

That the influence of the vessel wall is so closely similar for the normal and the sensitised reaction can be accounted for by the fact that step (7) of the above scheme is common to both.

6. *Comparison of Nitrous Oxide Sensitisation with Ammonia Sensitisation.*—Hydrogen–oxygen mixtures at 500° are sensitised by small amounts of ammonia, which causes an autocatalytic reaction ending in explosion (Williamson and Pickles, *Trans. Faraday Soc.*, **1934**, **30**, 927). The real sensitiser can be shown to be formed by interaction of ammonia with chain carriers of the hydrogen–oxygen reaction. All the facts were found to be consistent with the hypothesis that formation of nitric oxide is responsible for the sensitisation, except for one apparent anomaly. Small quantities of nitric oxide added initially to the system appeared not to shorten the time required to build up the critical concentration of the sensitiser. Repetition of the earlier work has now confirmed all the previous results, except this anomalous one. It now appears that the amounts of nitric oxide added initially were enough to cause partial ignition, difficult to observe, and that the subsequent measurement of the time to explosion referred to a system with quite different concentrations. If the amount of nitric oxide added is sufficiently small, the expected shortening of the time to explosion can in fact be observed. There is thus now no reason to doubt that nitric oxide is the sensitiser in both cases. From nitrous oxide it is formed by the action of hydrogen atoms, and from ammonia by the action of oxidising chain carriers such as O, OH, or HO_2.

7. *Note on the Unsensitised Hydrogen–Oxygen Reaction.*—In the course of these experiments the following additional information about the normal hydrogen–oxygen reaction has been obtained :

(*a*) The influence of deuterium oxide on the upper limit is almost identical with that of steam. Fig. 1 shows that this influence, relative to that of other gases, is greater than would be expected from the diffusion coefficients, and indicates that there is a specific influence on the chain-starting or -stopping processes.

(*b*) The activating influence of water on the silica wall is confirmed, Fig. 4 (*a*) showing how it may be controlled by evacuation of the bulb at a high temperature. Curves 1 and 5 were obtained after this treatment, a progressive activation by steam having been observed in the meantime (curves 2, 3, and 4).

(*c*) More complete removal of all traces of water vapour and more rapid working show that earlier values for the upper explosion limit, which is very sensitive to traces of water, should be somewhat increased. The new value at 550° is 128 mm.

[*Received, February* 22*nd*, 1940.]